PATENT SPECIFICATION

(11) 1368 230

(21) Application No. 35663/72 (22) Filed 31 July 1972
(31) Convention Application No. 167 513 (32) Filed 29 July 1971 in
(33) United States of America (US)
(44) Complete Specification published 25 Sept. 1974
(51) International Classification C23G 1/12
(52) Index at acceptance C7E 3B
(19)

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(54) COMPOSITIONS AND PROCESSES FOR DEOXIDIZING ALUMINIUM SURFACES

(71) We, AMCHEM PRODUCTS, INC., a Corporation organised under the Laws of the Commonwealth of Pennsylvania, United States of America, of Brookside Avenue, Ambler, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions and processes for deoxidizing aluminium surfaces. More particularly it relates to compositions and processes for deoxidizing and desmutting aluminium surfaces before finishing operations. The term "aluminium" as employed herein includes pure aluminium, commercial grade aluminium containing small amounts of impurities and aluminium alloys.

Aluminium surfaces are usually coated with surface corrosion (an oxide film) formed by atmospheric oxidation of the metal surface. Before the aluminium surface can undergo a finishing treatment such as spot welding, conversion coating, anodizing or painting, the oxide film and surface corrosion must be removed, since if the oxide film is allowed to remain on the surface, it interferes with the finishing treatment. For example, a protective coating such as an anodized coating or chemical conversion coating will not deposit uniformly on such an aluminium surface, and its adhesion to the surface will be very poor. Furthermore, a fine particulate material, known as smut, is often found on aluminium surfaces which have been treated with alkaline etching or cleaning solutions. When the cleaning or etching solution reacts with the aluminium surface, any metals with which the aluminium is alloyed remain behind on the surface in the form of their salts—these salts being the smut. In such cases a desmutting operation is necessary before any finishing treatment can be applied to the aluminium surface.

A variety of treatments and processes have been tried for removing oxide films and smut deposits from aluminium surfaces, but in most of these prior art processes the presence of noxious materials in the effluents from the baths has been a major problem. These prior art deoxidizing solutions contain chromates, dichromates, or nitric acid which create waste disposal problems, handling problems, and difficulties due to the corrosive action of the solutions on the equipment employed. In addition, these solutions tend to contaminate the baths used in the subsequent finishing operations. When chromates or dichromates are employed, the chromate must be neutralized and reduced before the solutions can be discarded.

Furthermore, the conventional deoxidizing and desmutting solutions tend to attack the aluminium surface severely as well as the aluminium oxide film and smut deposits. This attack on the aluminium surface is sufficient to cause a build-up of undesirable metal ions in the treatment solution, which shortens its useful life. Finally, often the deoxidizing and desmutting solutions cause further smutting of the aluminium surface. For example, when the surface of a copper-containing aluminium alloy is deoxidized, the surface often becomes covered with a black speckled smut consisting of the alloyed copper and copper oxide. The presence of the residual smut decreases the protection given to the aluminium surface by any subsequent finishing operation. Most present day deoxidizing and desmutting solutions are discarded because of residual deposits and the build-up of undesirable metal ions in the solution well before the deoxidizing and desmutting properties of the solution have been expended—which is, of course, extremely wasteful and uneconomic.

It is an object of this invention to provide an improved deoxidizing composition for aluminium surfaces and a process for using it. More particularly, this invention seeks to provide a chrome-free deoxidizing composition for aluminium which does not result in residual deposits on the surface or a build-up

of undesirable metal ions in the treating bath and which therefore has an improved useful life.

Accordingly, this invention provides a composition for use in the deoxidizing of aluminium surfaces comprising a fluoride and thiourea, together with ferric ion and/or a combination of ferrous ion and an oxidizing agent capable of oxidizing ferrous ion to ferric ion.

This invention extends to compositions in the form of both solutions ready for use and the solid or liquid concentrates used for making up such solutions. In either case, it is preferred that there be from 0.05 to 0.75 parts by weight of fluoride ion, and from 0.01 to 0.25 parts by weight of thiourea in the composition for each part by weight of iron ion. The fluoride ion can be present in the composition in the form of hydrofluoric acid or any soluble salt thereof, but it is preferably present as an alkali metal fluoride, most desirably sodium fluoride. The iron can be present in the form of any soluble ferrous or ferric salt. Preferably, ferric sulphate or ferrous sulphate should be employed. If a ferrous salt is used, an oxidizing agent capable of oxidizing ferrous ion to ferric ion must also be present. Examples of such oxidizing agents are persulphate, hydrogen peroxide, and permanganate; desirably persulphate or hydrogen peroxide is used in the compositions of this invention. The persulphate can conveniently be added to the composition in the form of an alkali metal or ammonium persulphate salt, most desirably, ammonium persulphate, sodium persulphate, or potassium persulphate.

Where the composition of this invention is in the form of an aqueous solution ready for application to the aluminium surface to be deoxidized, it is preferred that it contain from 5 g/l to 21 g/l of ferric ion, from 0.05 g/l to 3.0 g/l, most desirably 0.1 g/l to 2 g/l of thiourea and from 0.5 g/l to 2.0 g/l of fluoride ion. (It will, of course, be appreciated that on adding a solid composition containing ferrous ion and an oxidizing agent to water, ferric ion will be generated). The pH of the deoxidizing solution is preferably from 0.1 to 1.8; if necessary a strong mineral acid, such as sulphuric acid, can be added to the solution to adjust the pH to within this range. It should be noted, however, that in some instances, the deoxidizing solution can be prepared by adding the deoxidizing composition or concentrate to water without any acid being added. The resultant deoxidizing solution will naturally assume a pH less than 1.8, thereby allowing the deoxidizing process to be initiated and continue in the absence of strong acid.

The compositions of this invention may also be in the form of dry compositions suitable for making up the aqueous deoxidizing solutions by adding to water or aqueous acid, or for replenishing such solutions as they become depleted during use.

If the dry deoxidizing composition contains a ferrous salt, the ferrous salt and the oxidizing agent should not be stored in the same dry composition, since under these circumstances it has been found that the oxidant can decompose. The oxidizing agent may be mixed with the composition immediately before it is used to make up the solution, or it may be added to the solution separately from the ferrous salt. Desirably the ferrous salt and the oxidizing agent will be added to the aqueous acid solution in stoichiometric amounts so that essentially all the ferrous ion is oxidized. Two dry compositions can be used for making up the deoxidizing solution, one containing the ferrous salt, either alone or together with other constituents, and the other containing the oxidizing agent, either alone or with other constituents. When a dry make-up composition including a ferrous salt is used the best results are obtained with one dry admixture containing the ferrous salt and thiourea, and a second dry admixture containing the oxidizing agent and the fluoride.

Of course, when the composition contains a ferric salt, a single composition including all the necessary components can be used to make up the deoxidizing solution.

Finally, the compositions of this invention may also take the form of liquid concentrates suitable for dilution with water or aqueous acid to give the deoxidizing solutions ready for use.

Whatever form they take—whether they be solutions ready for use, dry compositions or liquid concentrates—the compositions of this invention will desirably incorporate surface activators, wetting agents, or detergents. Such materials enhance the cleaning performance and surface contact of the solution. These contact and cleaning agents are preferably present in the deoxidizing solution ready for use in an amount from 0.01% to 0.1% by weight.

This invention also provides a process for the deoxidizing of an aluminium surface, in which the surface is contacted with an aqueous acidic coating composition of this invention containing ferric ion, fluoride ion and thiourea.

During this process the aluminium substrate is preferably brought into contact with the deoxidizing solution by immersing it in the solution or by spraying the solution on to the surface. In order to remove effectively the oxide and smut from the aluminium surface, the contact time between the surface and the solution should be desirably from 30 seconds to 15 minutes. Th optimum contact time depends upon the type of aluminium alloy and the amount of smut, oxide, and surface corrosion to be removed. The deoxidizing process

is preferably operated at a temperature of from 60° F. to 150° F., most desirably from 60° F. to 90° F.

During operation of the process, both ferric and ferrous ions are present in the solution, and ferric ion is continuously being converted to ferrous ion. In order to allow the deoxidizing process to continue, it is necessary to maintain the concentrations of ferric ion. Thus it is desirable that the solution be replenished with an oxidizing agent capable of oxidizing ferrous ion to ferric ion. Suitable oxidizing agents include persulphates, peroxides, and permanganates. The amount of oxidizing agent which should be added to replenish the solution depends on the rate at which the ferric ion is being reduced. When the ferric ion concentration is depleted to below 6.0 g/l, it becomes very desirable to replenish the deoxidizing solution with the oxidizing agent.

The amount of oxidizing agent which must be periodically added to replenish the deoxidizing solution can be determined by well known methods. For example, the ferrous ion content can be determined directly by titration with a potassium permanganate solution. The amount of oxidizing agent added should be stoichiometrically equal to the amount of ferrous ion present. Alternatively, the ferric ion content can be determined, and that amount subtracted from the total iron content in the bath to find the ferrous ion concentration. Simple titration methods known to the art, such as iodometric titrations, can be employed in order to determine the ferric ion concentration.

The etching of the aluminium surface during the process of this invention causes small amounts of aluminium to enter the bath as aluminium ion. As aluminium builds up in the solution, the fluoride ion present is depleted, since soluble complex aluminium fluorides are formed. It has been found that in order to keep the solution working properly, it is important to regulate the concentration of fluoride in the solution relative to the concentration of aluminium therein so that the concentration of free fluoride ion is maintained at the desired level. Unless the fluoride concentration is increased as the aluminium content of the deoxidizing solution increases, the amount of free fluoride ion in the bath will be insufficient and the deoxidizing ability of the solution will be reduced.

It has been found that as ferric ion is reduced to ferrous ion during operation of the process, aluminium enters the bath as aluminium ion at a molar ratio of about one mole of aluminium for every three moles of ferrous ion produced. Thus, the ferrous ion concentration is an indication of the amount of aluminium which has complexed with the fluoride ion in the bath, and therefore, the amount of fluoride which should be added to the bath can be determined from the amount of ferrous ion in the solution.

A small amount of ferric ion is lost from the solution by drag-out (physical removal of the treatment solution on the metal surface) during operation of the process and should preferably be replaced with an appropriate amount of ferric or ferrous salt.

During operation of the process of the present invention, there is little or no evolution of hydrogen from the deoxidizing solution, this indicates that little reduction of hydrogen ion occurs. The strong mineral acid present in the deoxidizing solution is therefore not depleted to any significant extent during the operation of the process, and it is not usually necessary to replenish the solution with acid. Should the acid content of the deoxidizing solution become depleted due to drag-out, small additions of acid may be made to restore the pH of the solution to the desired level. The pH of the deoxidizing solution should be maintained in the range of from 0.1 to 1.8.

Due to the constant release of metal ions into the bath and such factors as drag-out, the thiourea in the solution is depleted, and it is very desirable to replenish the deoxidizing solution with thiourea. Since it sequesters undesirable metal ions the thiourea is depleted at a rate different from the other constituents of the solution. If all the materials necessary for replenishment are being added as a single replenishing composition, it may be necessary for the thiourea to be added separately to the solution, in addition to its inclusion as a constituent in the replenishing composition.

The replenishment of the solution during operation of the process of this invention is conveniently effected by adding to the solution an appropriate quantity of a dry composition or liquid concentrate of this invention.

Before being treated by this deoxidizing process, the aluminium surface should preferably be cleaned to remove oils, grease, and dirt. This cleaning can be effected by any of the cleaning operations known in the prior art, but the preferred method is to use a vapour degreasing process employing an organic solvent such as trichloroethylene, possibly followed by a mild alkaline cleaner. The mild alkaline cleaner will preferably contain an inhibitor to prevent excessive pitting of the aluminium surfaces. The metal surface is desirably rinsed after cleaning and is then ready to be treated with the deoxidizing solution.

An alternative cleaning step for aluminium alloy castings uses an alkaline cleaner to remove oils and mould lubricants, followed by an alkali etch bath. This is desirably followed by an appropriate rinse before the casting is treated by the process of this invention.

After deoxidizing the aluminium surface should preferably be rinsed with water to ensure that all the deoxidizing solution has been removed therefrom. The surface can then be dried in an oven or with hot air and prepared for any subsequent finishing treatment. The deoxidized, rinsed and dried surface can be treated to deposit a protective or decorative coating, such as a chromate conversion coating or an anodized coating thereon, and thanks to the process of this invention, the coating produced will possess excellent adhesion and will be useful as a base for a subsequent siccative finish.

This invention naturally extends to an article having an aluminium surface treated by the process of the present invention.

Using the compositions and process of the present invention more effective deoxidizing of the aluminium surface is accomplished with slightly increased and controlled surface etching; the oxide film and smut are effectively removed whilst virtually no residues remain on the surface after deoxidizing. Due to the unique interactions of the constituents of the deoxidizing solutions, more effective deoxidizing is achieved without any resultant drawbacks, and the solutions have a long operating life.

The controlled and increased etching of the aluminium surfaces achieved by the deoxidizing solutions of the present invention is effected without recourse to hydrogen ion attack of the surface which is extremely difficult to control. The strong acid, such as sulphuric acid which is employed in the deoxidizing solution in order to adjust its pH is not depleted except by drag-out, and little or no acid replenishment is necessary during operation of the process.

The interactions of the constituents in the present deoxidizing solution are complex and whilst the following theoretical explanation is believed to be correct, the invention is in no way limited by this explanation, which has been deduced from observations and analyses made during operation of the process.

The fluoride ion in the solution tends to increase the etch rate, while ferric ion significantly decreases the etch rate, to a degree approximately equal to the accelerating effect of the fluoride ion. Thus, the presence of ferric ion in the solution along with fluoride ion lowers the etch rate as compared with a solution in which fluoride ion is present without ferric ion.

Apart from lowering the etch rate the ferric ion appears to aid the attack on the oxide film and the removal of smut deposits presumably by a redox mechanism.

The interaction of thiourea with the ferric ion in the deoxidizing solution contributes to an increase in the etch rate since the presence of thiourea in the deoxidizing solution decreases the inhibiting power of ferric ion on the etch rate.

The controlled increased etch and improved deoxidizing due to this interaction is achieved without excessive pitting and non-uniformity of surface appearance. In this way, controlled additions of thiourea to the bath allow the fluoride ion to slightly increase the etch rate. The amount of thiourea in the solution is critical since excess thiourea may not interact with the ferric ion and could cause a decrease in the etch rate.

Even though the increase in etch rate results in more metal ions entering the deoxidizing solution, the presence of thiourea prevents the deposition of metals (with which the aluminium is alloyed) on the surface. The thiourea acts as a complexing agent, thus preventing the metal ions from redepositing out onto the metal surface. For example, when a copper/aluminium alloy is cleaned, copper is released into the deoxidizing solution. As the copper content in the solution reaches a high level, metallic copper tends to deposit on the aluminium surface. The thiourea sequesters sufficient copper ions in the solution to prevent copper deposition on the surface, thereby reducing interference with the deoxidizing process. Thus, the thiourea, by sequestering undesirable metal ions, increases the working life of the deoxidizing solution.

Thus, the thiourea should be present in an amount sufficient to sequester significant amounts of the metal ions which enter the solution during use and in an amount sufficient to interact with the ferric ion in the deoxidizing solution, and as stated above, it should preferably be present in an amount from 0.05 g/l to 3 g/l. It is especially preferred that there be from 0.1 g/l to 2.0 g/l of thiourea in the deoxidizing solution. If the amount of thiourea in the solution exceeds 3.0 g/l, there is excess thiourea present over and above that which is necessary to both complex undesirable metal ions and to interact with ferric ion and fluoride ion, and the solution becomes difficult to control properly.

In order that this invention may be more easily understood, the following examples of compositions and processes of the invention are now given, though by way of illustration only.

Example 1.

Formulations 1 and 2 are examples of compositions, one containing a ferrous salt and the other containing an oxidizing agent, which can be mixed and used to prepare an aqueous acidic deoxidizing solution of this invention.

Formulation 1.

	% by weight
Ferrous sulphate heptahydrate	99.51
Thiourea	0.2
Wyandotte Pluronic F127 (nonionic wetting agent)	0.29
	100.00%

"Wyandotte" and "Pluronic" are Registered Trade Marks.

Formulation 2.

	% by weight
Sodium persulphate	93.60
Sodium fluoride	6.40
	100.00%

Example 2.

Formulations 3 and 4 are examples of single concentrates of this invention containing a ferric salt which can be added to an aqueous acid to prepare a deoxidizing solution. Formulation 3 is a liquid concentrate, whilst Formulation 4 is a dry powder.

The ferric sulphate employed in this and the other Examples except Example 7 was a commercial hydrated product containing approximately 71% by weight of ferric sulphate, together with approximately 12.4% water of hydration, 3 to 4% of insoluble impurities and 4 to 5% of ferrous sulphate, the ferrous sulphate being present in a hydrated form.

Formulation 3.

	% by weight
Ferric sulphate	34.11
Hydrofluoric acid (70%)	0.51
Thiourea	0.41
Wetting agent (Wyandotte RA43)	0.20
Water	64.77
	100.00%

Formulation 4.

	% by weight
Ferric sulphate	94.80
Sodium fluoride	4.60
Thiourea	0.25
Surfactant	0.35
	100.00%

Example 3.

Formulation 5 is a dry replenishing composition and Formulation 6 is an aqueous replenishing concentrate either of which can be employed when necessary during operation of the process of this invention. Formulation 6 does not contain thiourea since such a concentrate containing thiourea would be unstable. When this replenishing concentrate is employed, the thiourea replenishment must be effected separately.

Formulation 5.

	% by weight
Sodium persulphate	88.84
Sodium fluoride	10.52
Thiourea	0.64
	100.00%

Formulation 6.

	% by weight
Hydrogen peroxide	8.75
Hydrofluoric acid (70%)	3.04
Water	88.21
	100.00%

Example 4.

Formulations 7 and 8 are compositions which can be employed together to prepare a deoxidizing solution by their addition to water without any strong mineral acid being added.

Formulation 7.

	% by weight
Ferrous sulphate heptahydrate	99.51
Thiourea	0.2
Wetting agent	0.29
	100.00%

Formulation 8.

	% by weight
Sodium persulphate	91.12
Sodium fluoride	8.88
	100.00%

Example 5.

A dry deoxidizing composition was prepared by mixing 102.5 grams of ferrous sulphate heptahydrate, 0.2 grams of thiourea, and 0.3 grams of a wetting agent (Wyandotte Pluronic F 127), and grinding the admixture until it became a fine powder. A second dry composition was prepared by mixing 37.2 grams of s dium persulphate with 3.6 grams of sodium fluoride and grinding the admixture until it was a fine powder. The two dry compositions were added to 1 litre of aqueous acid containing 5% by volume of 66° Bé sulphuric acid to form a deoxidizing solution of this invention.

Example 6.

A deoxidizing composition of this invention was prepared by mixing 74 grams of

ferric sulphate, 0.2 grams of thiourea, 0.3 grams of wetting agent (Wyandotte Pluronic F 127), and 3.6 grams of sodium fluoride. The deoxidizing composition was added to 1 litre of aqueous acid containing 5% by volume of 66° Bé sulphuric acid to form a deoxidizing solution of this invention.

Example 7.

A deoxidizing liquid concentrate of this invention was prepared by adding 682 ml. of a commercially-available aqueous solution of ferric sulphate containing 50% by weight of ferric sulphate, 6.8 ml. of 70% hydrofluoric acid, 6.8 grams of thiourea, and 2.5 grams of Pluronic F 127, to 1 litre of water. 125 ml. of the deoxidizing concentrate was added to each litre of aqueous acid containing 5% by volume of 66° Bé sulphuric acid to form a deoxidizing solution of this invention ready for use.

Example 8.

A dry composition was prepared containing 96.5% by weight of ferrous sulphate heptahydrate, 3.38% by weight of sodium fluoride, and 0.12% by weight of thiourea and a deoxidizing solution was prepared by adding 8.9 lbs. of this composition to 83.3 gallons of aqueous acid containing 5% by volume of 66° Bé sulphuric acid; 3.1 lbs. of sodium persulphate was then added to give a deoxidizing solution of this invention.

3" × 10" Panels of 2024T3 alloy were first degreased with methyl alcohol, subjected to a mild alkaline cleaner for 10 minutes at 175° F., then removed from the alkaline cleaner and rinsed with water. The panels were immersed for 15 minutes in the deoxidizing solution prepared above at a temperature of 80° F. When they were withdrawn from the deoxidizing bath there were no visible smut deposits on their surfaces. After this treatment with the deoxidizing solution, the metal surfaces were rinsed with water to remove any remaining deoxidizing solution, and then given a protective chromate conversion coating.

Example 9.

An aqueous deoxidizing solution was prepared by using 103 grams of Formulation 7 above and 42 grams of Formulation 8 above per litre of water. The pH of the resultant deoxidizing solution was 1.72. No mineral acid was added to the solution and during operation of the deoxidizing process no additions of acid were made.

3" × 10" Panels of 2024T3 alloy were degreased in an organic solvent and were then cleaned in a mildly alkaline cleaning solution for 10 minutes at 175° F. The panels were rinsed with water and then immersed in the deoxidizing solution for 15 minutes at 80° F. After the deoxidizing had been completed, the aluminium surfaces showed a satisfactory surface etching without pitting and were free from smut.

Example 10.

Tests showing the superiority of compositions containing thiourea.

The following tests were performed to illustrate the superiority of the deoxidizing solutions of the present invention containing thiourea over similar solutions without thiourea. 2" × 3" Panels of 2024/T3 aluminium alloy were cleaned in an alkaline cleaning bath containing sodium meta-silicate, tetrasodium pyrophosphate, sodium carbonate and wetting agents for 10 minutes at 150° F. The panels were then rinsed in tap water and dried. After drying the panels were weighed before treatment with the deoxidizing solution.

The deoxidizing step was effected at a temperature of 78° F. and each panel was immersed in its solution for a period of 10 minutes. Etch rate determinations were made for three panels treated with each of the solutions listed in the Table below. After the deoxidizing treatment had been completed, the panels were rinsed, dried, and reweighed. The etch rates of each of the three panels and the average etch rate were calculated; the results are shown in the Table.

Baths 1, 2, 5, and 6 were prepared by adding dry compositions to aqueous acid containing 2.5% by volume of 66° Bé sulphuric acid to give the concentrations of ferric ion, fluoride ion, and thiourea shown in the Table. Baths 3, 4, 7 and 8 were prepared by adding dry compositions to aqueous acid containing 7.5% by volume of 66° Bé sulphuric acid.

Thiourea was omitted from baths 1, 3, 5 and 7 whereas in baths 2, 4, 6 and 8 thiourea was included in the dry deoxidizing compositions so that when these compositions were added to aqueous acid the concentration of thiourea in the baths was 0.4 g/l.

TABLE

Bath No.	Constituents	Concentration g/l	Etch rate in mils/hour × 10^{-3}			Average etch rate mils/hour × 10^{-3}
1 (Control	Fe^{+++} F^- Thiourea	7.0 0.82 —	11.75	11.32	11.71	11.59
2	Fe^{+++} F^- Thiourea	7.0 0.82 0.4	11.84	12.28	12.24	12.12
3 (Control)	Fe^{+++} F^- Thiourea	27.0 2.46 —	17.88	17.83	18.58	18.10
4	Fe^{+++} F^- Thiourea	27.0 2.46 0.4	23.09	21.79	22.48	22.45
5 (Control)	Fe^{+++} F^- Thiourea	27.0 0.82 —	6.60	6.36	6.47	6.47
6	Fe^{+++} F^- Thiourea	27.0 0.82 0.4	7.24	6.79	7.11	7.00
7 (Control)	Fe^{+++} F^- Thiourea	27.0 0.82 —	9.12	9.28	9.21	9.20
8	Fe^{+++} F^- Thiourea	17.0 0.82 0.4	10.17	10.15	10.24	10.19

The results in the Table illustrate that the addition of thiourea to the bath results in a slightly increased etch rate, thus allowing more effective deoxidation. After treatment with deoxidizing baths 2, 4, 6 and 8 the panels showed bright, smut-free surfaces.

WHAT WE CLAIM IS:—

1. A composition for use in the deoxidizing of aluminium surfaces, comprising a fluoride and thiourea together with ferric ion and/or a combination of ferrous ion and an oxidizing agent capable of oxidizing ferrous ion to ferric ion.

2. A composition as claimed in claim 1, in which there are from 0.05 to 0.25 parts by weight of fluoride ion per part by weight of iron ion.

3. A composition as claimed in either of the preceding claims, in which there are from 0.01 to 0.25 parts by weight of thiourea for each part by weight of iron ion.

4. A composition as claimed in any of the preceding claims, in which the fluoride ion is present as an alkali metal fluoride.

5. A composition as claimed in claim 4, in which the alkali metal fluoride is sodium fluoride.

6. A composition as claimed in any of the preceding claims, in which the iron is present as ferric sulphate and/or ferrous sulphate.

7. A composition as claimed in any of the preceding claims in which the oxidizing agent is a persulphate and/or hydrogen peroxide, and/or a permanganate.

8. A composition as claimed in claim 7, in which the persulphate is added as an alkali metal or ammonium persulphate salt.

9. A composition as claimed in claim 8, in which the alkali metal persulphate is sodium persulphate and/or potassium persulphate.

10. A composition as claimed in any of the preceding claims in the form of an aqueous acidic solution ready for application to an aluminium surface to be deoxidized and con-

taining from 5 g/l to 21 g/l of ferric ion.

11. A composition as claimed in claim 10, which contains from 0.05 g/l to 3.0 g/l of thiourea.

12. A composition as claimed in claim 11, which contains from 0.1 to 2 g/l of thiourea.

13. A composition as claimed in any of claims 10 to 12, which contains from 0.5 g/l to 2.0 g/l of fluoride ion.

14. A composition as claimed in any of claims 10 to 13, which has a pH of from 0.1 to 1.8.

15. A composition as claimed in any of the preceding claims, which also incorporates a surface activator and/or a wetting agent and/or a detergent.

16. A composition as claimed in any of claims 10 to 14 and in claim 15, in which the surface activators, wetting agents and detergents constitute from 0.01% to 0.1% by weight of the composition.

17. A composition for use in the deoxidizing of aluminium, as claimed in any of the preceding claims and substantially as described herein, with reference to the Examples.

18. A process for the deoxidizing of an aluminium surface, in which the surface is contacted with an aqueous, acidic coating composition as claimed in any of the preceding claims.

19. A process as claimed in claim 18, in which the aluminium substrate is brought into contact with the deoxidizing composition by immersing it in the solution or by spraying the solution on to the surface.

20. A process as claimed in claim 18 or 19, in which the contact time between the surface and the composition is from 30 seconds to 15 minutes.

21. A process as claimed in any of claims 18 to 20, which is operated at a temperature of from 60° F. to 150° F.

22. A process as claimed in claim 21, which is operated at a temperature of from 60° F. to 90° F.

23. A process as claimed in any of claims 18 to 22, in which, after a quantity of aluminium substrate has been deoxidized, the composition is replenished with an oxidizing agent capable of oxidizing ferrous ion to ferric ion.

24. A process as claimed in claim 23, in which the oxidizing agent used for replenishment is a persulphate and/or a peroxide and/or a permanganate.

25. A process as claimed in claim 23 or 24, in which the composition is replenished whenever the ferric ion concentration therein falls below 6.0 g/l.

26. A process as claimed in any of claims 18 to 25, in which, after a quantity of aluminium substrate has been deoxidized, the composition is replenished with an amount of fluoride ion proportional to the amount of aluminium which has entered the composition.

27. A process as claimed in any of claims 18 to 26, in which the composition is replenished with a ferric and/or ferrous salt.

28. A process as claimed in any of claims 18 to 27, in which the composition is replenished with acid in any amount sufficient to maintain the pH of the composition in the range of from 0.1 to 1.8.

29. A process as claimed in any of claims 18 to 28, in which, after treatment of a quantity of aluminium substrate, the composition is replenished with thiourea.

30. A process as claimed in claim 26, 27 and 29, in which the iron, fluoride and thiourea used for replenishment are added to the composition in the form of a dry composition and/or liquid concentrate as claimed in any of claims 1 to 17.

31. A process as claimed in any of claims 18 to 30, in which, before being treated by the deoxidizing process, the aluminium surface is cleaned to remove oils, grease, and dirt therefrom.

32. A process as claimed in claim 31, in which the cleaning is effected by a vapour degreasing process employing an organic solvent.

33. A process as claimed in claim 32 in which the organic solvent is trichloroethylene.

34. A process as claimed in claim 32 or 33, in which the vapour degreasing is followed by treatment with a mild alkaline cleaner.

35. A process as claimed in claim 34, in which the mild alkaline cleaner contains an inhibitor to prevent excessive pitting of the aluminium surface.

36. A process as claimed in claim 31, in which the cleaning is effected by use of an alkaline cleaner to remove oils and mould lubricants, followed by an alkali etch bath.

37. A process as claimed in any of claims 31 to 35, in which the metal surface is rinsed after cleaning and before being deoxidized.

38. A process as claimed in any of the preceding claims, in which, after deoxidizing, the aluminium surface is rinsed with water to ensure that all the deoxidizing solution has been removed therefrom.

39. A process as claimed in claim 38, in which, after rinsing, the surface is dried in an oven or by means of hot air.

40. A process as claimed in any of claims 18 to 39 and substantially as described herein, with reference to Examples 4 to 10.

41. An article having an aluminium surface treated by a process as claimed in any of claims 18 to 40.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.